

ANNUAL REPORT TO
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
FOR
THE CONTINUATION OF
MEASUREMENT OF HO₂ AND OTHER TRACE GASES IN THE STRATOSPHERE
USING A HIGH RESOLUTION FAR-INFRARED SPECTROMETER

NASA GRANT NAG5-9361

Annual Report No. 4

For the period 1 November 2003 to 31 October 2004

Principal Investigators: Wesley A. Traub and Kelly V. Chance

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Smithsonian Institution
Astrophysical Observatory
Cambridge, Massachusetts 02138

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Annual Report No. 3

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Measurement of HO₂ and Other Trace Gases in the Stratosphere Using a High Resolution Far-Infrared Spectrometer

1. Personnel Working Under this Grant During this Reporting Period

Dr. Wesley A. Traub (Principal Investigator)

Dr. Kelly V. Chance (Principal Investigator)

Dr. Kenneth W. Jucks (Co-Investigator)

Dr. David G. Johnson (Co-Investigator)

2. Status Summary

This report covers the time period 1 November 2003 to 31 October 2004. During this period we had one balloon flight, analyzed the data from the previous 2 flights, explored issues such as radical partitioning, stratospheric transport, and molecular spectroscopy and further developed our beamsplitter technology.

3. Recent balloon flights

Our balloon flight on September 23 and 24, 2004 was a very successful flight as far as spectral signal-to-noise, spectral range and length of flight. We had roughly 24 hours at float altitude, most of which provided useful data. During the latter part of the flight the JPL azimuth drive failed, which negatively affects the pointing of FIRS-2. But we believe that we can obtain accurate profiles from these spectra, by correcting for pointing uncertainties by using the 16 micron CO₂ band.

This flight also coincided with 2 Aura overpasses, one during the local afternoon and one at local 2:00 AM. FIRS-2 was operating nominally at both times and should provide good validation data for both MLS and TES. The data at both overlap times will extend from the balloon altitude down to roughly 10 km.

4. Instrument and Software Development

We have made further significant progress on the development of efficient broad-band beam splitters both for FIRS-2. We now have numerous germanium on polypropylene beam splitters that have nearly 50% reflection and 50% transmission over the range of 80 to 2000 cm⁻¹, with the exception of a small band from 1000 to 1100 cm⁻¹. We have used these on our last three balloon flights. With the most recently constructed beam splitters, we have reduced the compressive stress features that prove difficult to keep flat over a long period of time while mounted. These beam splitters are also being constructed for the FIRST project and numerous now exist for that project as well that have good spectral response and low stress.

Before the last balloon flight, we replaced the cornercubes in the FIRS-2 spectrometer. This was done because we discovered over the past year that they were the cause of the low instrument response we have always observed near 600 cm^{-1} . The old cornercubes were gold surface glass mirrors that has a MgCl_2 protective overcoat, which was the standard far infrared overcoat material when they were constructed. While doing mirror tests for FIRST, we discovered that mirrors with this overcoat had the same absorption feature that we have been observing in FIRS-2. The new cubes, coated with Y_2O_3 , do not have any absorption features throughout the FIRS-2 spectral range and operated well during our last balloon flight.

On the last flight, the recovery crew stepped on a sensitive part of the instrument and broke a key weld. This is currently being fixed in a way that will prevent this from happening in the future. While the instrument is apart, we are developing a better technique for aligning the instrument. This will all be done well before the next balloon flight.

We have completed the software conversion for processing the FIRS-2 balloon flight data. This allows for quicker analysis of the data than in the past and allowed us to get our data from the 2002 and 2003 flights into the BOS data archive at NASA Ames in a timely fashion. We also now have a functioning down range GSE system using old DOS computer equipment. This was set up during the 2004 flight but was not needed since the flight corresponded well with the stratospheric turnaround.

5. Data Interpretation

We have continued our collaboration with Ross Salawitch, Lori Kovalenko and Geoff Toon of JPL on the photochemistry of HOCl using both FIRS-2 and MkIV retrievals of HOCl , along with FIRS-2 retrievals of HO_2 . Currently we get different comparisons between measured and modeled values between the two instruments and we are trying to determine if this is caused by differences in errors for the retrievals of the two instruments, differences in the retrieved constraints used in the models, or differences caused by the fact MkIV retrieves at sunrise and sunset as opposed to the day/night retrievals of FIRS-2.

The retrievals of H_2O_2 from the past balloon flights have significantly better signal to noise compared to past flights of FIRS-2, especially for the night time data. The data from the 2003 flight show a clear diurnal variation in H_2O_2 in the middle stratosphere that is not expected based on currently known photochemistry. The data during the daytime are consistent with the model/measurement comparisons shown in *Christensen et al.* [2002] for FIRS-2 data where even with the new rates for the HO_2+HO_2 reaction, the middle stratospheric H_2O_2 were low compared to the model during the day. The night data are closer to the model calculations, consistent with the sunset data of MkIV. We will use the data from the 2004 flight to confirm these results and write a paper on the findings.

During the recent flights, we have extended our retrievals to roughly 4 km below the tropopause. Of the molecules that can be retrieved down to that altitude, the most interesting are the four main isotopes of water vapor, ozone, and acetone. Upper tropospheric ozone and water are important targets for Aura and the isotopic fractionation gives additional science that cannot be provided by Aura itself. Acetone has only been observed in

the upper troposphere via aircraft mass spec in situ data. Our acetone observations are the first remote sensing observations of this molecule. The band falls at a frequency that is unique to FIRS-2 among current remote sensing instruments.

We have submitted a paper that was recently accepted to JGR-Atmospheres on mesospheric O^3P with comparisons to models. We use the far infrared transition of this line to retrieve mesospheric radiances and compare this with that from mesospheric models [Mlynczak et al, 2004]. The comparison with the models is good to within the measurement uncertainties (10%) and is not consistent with similar comparisons from CRISTA at higher altitudes.

6. Satellite Validation

The past balloon flight had very good overlap with the footprints of MLS and TES on Aura. We will get this data to these validation teams as soon as we are confident in the results. These results will include H_2O , O_3 , HCl , $HOCl$, HO_2 , OH , $CFC11$, $CFC12$, N_2O , NO_2 , HNO_3 , N_2O_5 , and H_2O_2 , all of which are target molecules for Aura.

5. Publications, Presentations, and References

Christensen, L. E., M. Okumura, S. P. Sander, R. J. Salawitch, G. C. Toon, B. Sen, J.-F. Blavier, and K. W. Jucks, Kinetics of $HO_2+HO_2 \rightarrow H_2O_2 + O_2$: Implications for Stratospheric H_2O_2 , *Geophys. Res. Lett.*, 29, 1299, 2002.

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